Spectrophotometric Determination of Micro-amounts of Aluminium in Iron and Steel with Chrome Azurol S

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Synopsis

Fundamental experiments were carried out to determine the micro-amounts of aluminium by spectrophotometry, using chrome azurol S, a reagent used in complexometric titration of copper, zirconium and aluminium. By this new method, most part of the iron content was separated by methyl isobutyl ketone, and the remaining iron and copper was masked by thioglycolic acid and after adjusting the pH to 5.6–6.8, the absorbance of the aluminium chelate compound was measured at 550 mμ. This method requires only a few reagents and does not need warming for promoting coloration, nor does it require the protecting colloid in contrast with the aluminon method. Since this reagent presents very sensitive color reaction even in micro-amounts of aluminium, 0.002 to 0.1 per cent of it can be determined with good reproducibility.

I. Introduction

The previous method for photometric determination of a trace amount of aluminium in iron and steel has utilized aluminon and oxine-benzene extraction. The aluminon method requires a long time for electrolysis to separate iron and other elements from aluminium and its sensitivity is not so good. In oxine salt-benzene extraction method, iron and other elements can be masked by potassium cyanide, being not separated. On the other hand, when the amount of aluminium is very small, electrolytic separation will be required which, however, requires a long time as in the aluminon method. Chrome azurol S has been used as a complexometric titration reagent for aluminium[1] and a report has been published on metal ions which react on this reagent.[2] A good result was obtained by using this reagent for photometric determination of aluminium in iron and steel, details of which will be given below.

II. Reagents and apparatus

1. Reagents

0.1 per cent Solution of Chrome Azurol S : A solution of 0.1 g of chrome azurol S dissolved in 100 ml of water was used. This reagent is stable and the solution can be used for at least one week.

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* The 1024th report of the Research Institute for Iron, Steel and Other Metals. Reported in Japanese in the Journal of the Japan Institute of Metals, **24** (1960), 32.

(1) M. Theis, Z. anal. Chem., **144** (1955), 106, 275.

(2) T. Matsuo, reported at the Meeting of The Japan Society for Analytical Chemistry, (1958), October.

10 per cent Solution of Thioglycolic Acid: Thioglycolic acid (Special Grade) was diluted to 10 times of volume with water and stored in a colored bottle.

Methyl Isobutyl Ketone: First grade for chemical use.

Standard Aluminium Solution: A few drops of nitric acid was added to a solution of 0.5 g of metallic aluminium dissolved in hydrochloric acid (1+1) to effect oxidation and the solution was diluted to 1 l after cooling. A definite amount was taken from this solution and concentration of aluminium was determined by the gravimetric method, using oxine. Solutions of iron (III), manganese (II), chromium (III) and (VI), molybdenum, copper, lead, zinc, cadmium, magnesium, calcium, titanium (III) vanadium, tungsten, nickel, cobalt, tin, beryllium, and zirconium were prepared to examine the effect of coexisting elements.

2. Apparatus

Hitachi Photoelectric Spectrophotometer Model EPU-2 with 10 mm cell and Tōa Dempa HM-5 Glass-electrode pH-meter were used.

III. Experimental

1. Absorption curve

Chrome azurol S was first introduced by Theis and others[1] as a reagent for aluminium, copper, and zirconium. This reagent, a kind of pH indicator, is yellow below pH 4 and reddish orange at pH 4. It reacts reversibly on aluminium at above pH 5 and forms a blue chelate compound but the pigment itself is yellow at this pH so that a distinct color change is observable. Fig. 1 shows absorption curves of these colors. The blue color of the aluminium chelate compound has a maximum absorption at 550 mμ and its molecular absorption coefficient is 59.300, indicating sensitive reaction to aluminium. For this determination, 0.5, 20, and 50 μg of aluminium was placed in a measuring flask, 1.9 ml of 0.2 M acetic acid and 1.8 ml of 0.2 M sodium acetate were added, followed by 2 ml of 0.1 per cent chrome azurol S solution, and the whole was diluted to 100 ml with water.

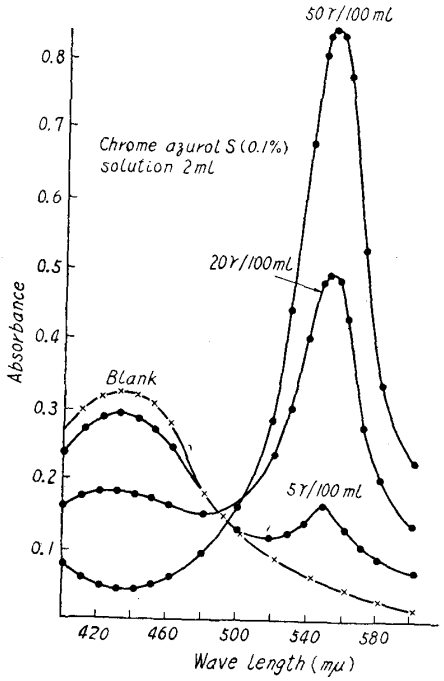

Fig. 1. Absorption spectra of the dye and its Al chelate compound.

2. Relationship between pH and absorbance

By using a solution of aluminium 10 μg /100 ml (3.72×10^{-6}M), pH of the solution was varied with the foregoing buffer solution and their absorbance was measured at 550 mμ. Results obtained are shown in Fig. 2. Absorbance of

aluminium chelate compound shows constant value at pH 5.6~6.8 and color of the reagent itself in this pH range is yellowish orange.

3. Amount of the reagent added

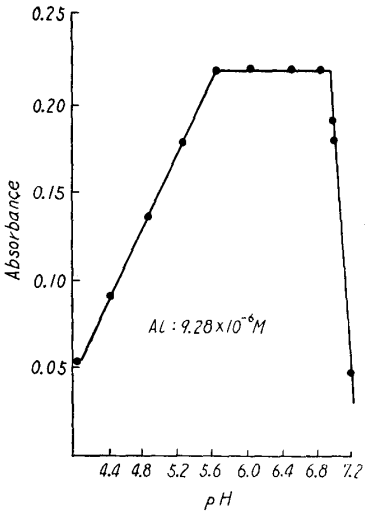

Fig. 2. Effect of pH on absorption of Al chelate compound at 550mμ.

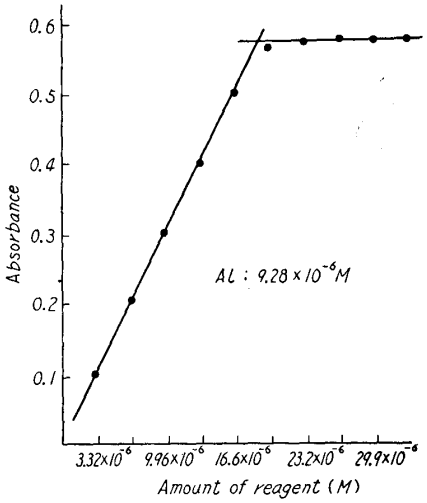

Fig. 3. Effect on absorption by varying the amount of reagent.

The amount of the reagent to be added was examined by molar ratio method. Various amount of 0.02 per cent chrome azurol S solution were added to the solution of 25μg/100 ml of aluminium (9.28×10^{-6} M) and absorbance of the solution was measured at pH 5.6. As shown in Fig. 3, the chelate compound is formed in 1 : 2 of molar ratio of aluminium to chrome azurol S, and addition of 2 ml of 0.1 per cent chrome azurol S solution is sufficient when the amount of aluminium is below 30 μg.

4. Stability of aluminium chelate compound

In order to examine the stability of aluminium chelate compound, pH of the solution was adjusted after addition of the reagent, the amount of solution was brought to 100 ml, and the change in the absorption of this solution was measured at definite intervals. As shown in Table 1, the absorbance reaches a constant value after approximately 20 minutes and is stable for subsequent 2 hours. The reagent itself is also stable and can be preserved for use.

5. Relationship between aluminium concentration and absorbance

In a 100-ml measuring flask, 0–30 μg of aluminium was placed, 0.5 or 10 ml each of 0.2 M acetic acid and sodium acetate solutions were added (pH 6), followed by 2 ml of 0.1 per cent chrome azurol S solution, and the whole was brought to 100 ml with water. The absorbance of the solution was measured at 550 mμ to obtain the relationship between the amount of aluminium and absorbance. As shown in Fig. 4, a linear relationship, following the Beer's law, was found to hold good.

6. Effect of coexisting elements

(i) Cations

Table 1. Stability of color of Al chelate compound.

Time (min.)	Absorbance	
	Blank	Al chelate against blank
5	0.032	0.217
10	0.029	0.233
20	0.029	0.246
30	0.028	0.247
40	0.028	0.248
50	0.028	0.249
60	0.025	0.250
70	0.025	.0250
80	0.025	0.250
90	0.023	0.247
100	0.023	0.248
110	0.023	0.249
120	0.022	0 246

Al : 3.72×10^{-6} M, Chrome azurol S : 0.1% solution 1 ml, pH, 6.0

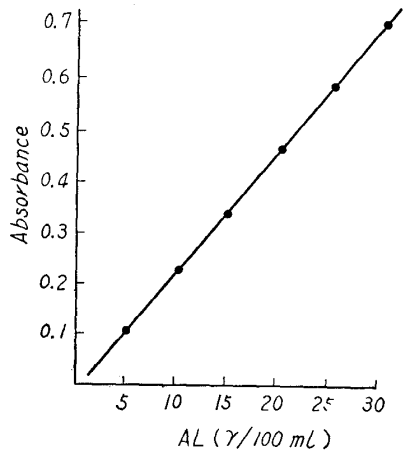

Fig. 4. Calibration curve.

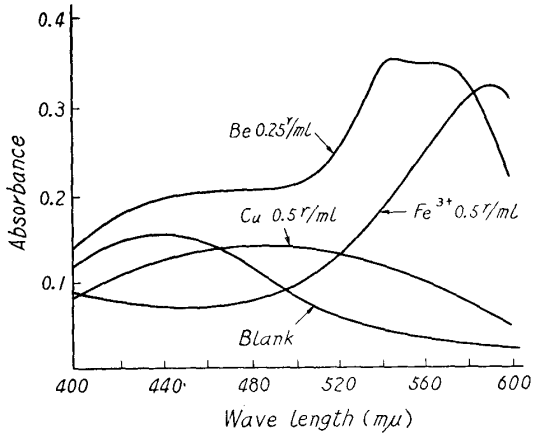

Fig. 5. Absorption spectra of chelate compounds of Fe^{3+}, Cu and Be at pH 6.0.

Iron (III) and copper are known to react with the reagent during titration of aluminium as reported by Theis[3], hence, examinations were made on this point. As shown in Fig. 5, both these ions form blue chelates with the reagent and show absorption in the same wave length of aluminium so that they interfere to a great extent. Beryllium is not usually present in iron and steel, and would not be a problem. Molecular absorption coefficient of iron (III) at 550 mμ is 33,500 and it reacts sensitively on the reagent, so that it must be completely reduced to iron (II), masked, or removed. The cations which do not affect this reaction are manganese, chromium (VI), molybdenum, lead, zinc, cadmium, magnesium, calcium, tungsten, vanadium, and phosphorus, there being no effect if these elements are present in around 10 mg to 10μg of aluminium. Chromium (III) and nickel have no effect below 1 mg and cobalt below 3 mg.

(3) A. Musil and M. Theis, Z. anal. Chem., **144** (1955), 427.

Interfering elements are, besides the above-mentioned iron (III), beryllium, copper, tin, titanium, thorium, and zirconium. Tin can be separated as metastannic acid. Titanium can be removed after hydrolysis or the solution was brought to 3~4N hydrochloric acid concentration, cupferron solution was added, and extracted with benzene-chloroform or benzene-ether mixture (1 : 1)

(ii) Anions

Interfering anions are tartaric acid, citric acid, and their salts. Aluminium compounds of these acids are more firmly bonded than with chrome azurol S so that they cannot be added as a subsidiary chelate. Fluorides and hydrogen peroxide also interfere in this reaction but chlorides, sulfates, carbonates, thiosulfates, acetates, and sulfite do not affect this reaction.

7. Masking of iron (III) and copper by thioglycolic acid

As stated above, presence of iron (III) and copper interferes in this reaction by the formation of a blue chelate like aluminium. Masking effect was examined by the use of thiolgycolic acid and the results obtained are listed in Tables 2 and 3. As shown in these tables, copper is completely masked by thioglycolic acid,

Table 2. Masking effect of thioglycolic acid for copper.

Amounts of Cu (mg)	Absorbance	
	When not added	When added
0.10	0.033	–
0.20	0.095	0.002
0.30	0.175	0.003
0.40	0.194	0.002
0.50	0.235	0.003

Table 3. Masking effect of thioglycolic acid for ferric ion.

Amounts of Fe(III) (mg)	Absorbance	
	When not added	When added
0.20	0.249	0.014
0.40	*	0.015
0.60		0.011
0.80		0.033
1.00		0.030

* Chelate precipitates.

and Iron (III) is completely reduced to iron (II) in an acidic solution but the iron (II) is partly oxidized to iron (III) in a neutral solution near pH 6 and forms a violet complex salt with thioglycolic acid. Since the absorbance of this complex salt increases somewhat with the amount of iron (III) added, a majority of iron must be removed preliminarily. Table 4 shows the result obtained by reducting and masking residual small amount of iron with thioglycolic acid after the

Table 4. Masking effect of thioglycolic acid for iron after extraction of ferric ion.

Amounts of Fe (III) (g)	Amounts of methyl isobutyl ketone (ml)	Extraction times	Absorbance (550 mμ)
0.5	30	1	0.033
0.5	20	2	0.003
1.0	30	2	0.005
1.0	40	2	0.003
1.0	50	2	0.004

extraction of iron with methyl isobutyl ketone[4]. For this experiment, 0.5 g of electrolytic iron was dissolved in hydrochloric acid, oxidized to iron (III), and this was extracted with methyl isobutyl ketone after adjusting the concentration of hydrochloric acid to 7N. Nitric acid was added to acid layer and the solution was evaporated to dryness. The residue was dissolved in a small amount of hydrochloric acid; the solution was diluted to 100 ml, and of this solution, added with 1 ml of 10 per cent thioglycolic acid solution, and was adjusted to pH 6.0. This solution was diluted to 100 ml and its absorbance was measured at 550 mμ. Since the electrolytic iron used contained aluminium, chrome azurol S was not added. The above results showed that the use of methyl isobutyl ketone for extraction of iron was sufficient to remove the interference of iron (III).

8. Effect of thioglycolic acid on absorbance of aluminium chelate

Effect of the addition of thioglycolic acid on the absorbance of aluminium chelate was examined and, as shown in Fig. 6, the absorbance was found to de-

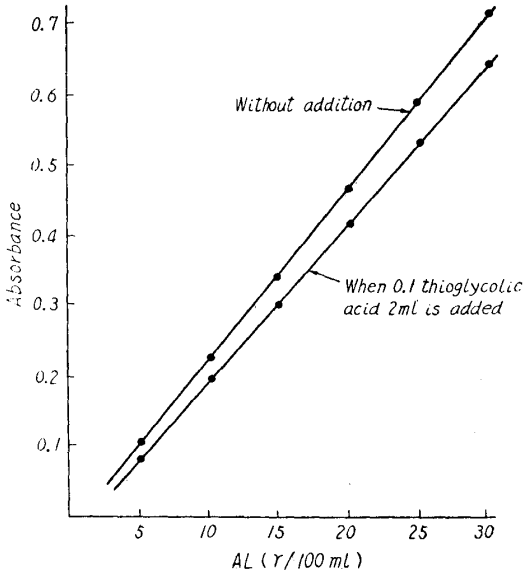

Fig. 6. Effect of addition of thioglycolic acid on absorption.

crease slightly. Consequently, it would be necessary to add the thioglycolic acid accurately in preparing the calibration curve.

(4) T. Furukawa, Y. Kakita and H. Goto, J. Chem. Soc. Japan, **79** (1958), 1513.

IV. Analytical procedure for iron and steel samples

To a solution of accurately weighed 0.5 g of the sample dissolved in 20 ml of hydrochloric acid (1+1), 1 ml of nitric acid is added, and the mixture is heated and evaporated to dryness. The cooled residue is warmed with 20 ml of hydrochloric acid (1+1) to dissolve the salts, and silica and insoluble substances are removed by filtration. The residue is treated with hydrofluoric acid, fused with potassium pyrosulfate and combined with the filtrate. The combined filtrate is concentrated to about 10 ml, transferred to a separatory funnel with 7N hydrochloric acid, and extracted with two 20-ml portions of methyl isobutyl ketone. The acid layer is poured into a beaker, evaporated to dryness, and boiled for 2–3 minutes with 5 ml of aqua regia. This is again evaporated to dryness, the residue is dissolved in 5 ml of hydrochloric acid (1+1), cooled, and transferred to a 100-ml measuring flask. The solution is brought to the mark with water and 10~20 ml of this solution is transferred to a 100-ml beaker. To this solution, 1 ml of 10 per cent thioglycolic acid and 2 ml of 0.1 per cent chrome azurol S solution are added in that order, the solution is adjusted to pH 5.6~6.8 with 0.2 M solution of acetic acid and sodium acetate, using the pH meter, and transferred to a 100-ml measuring flask. The solution is diluted to 100 ml with water, allowed to stand for 20 minutes, and absorbance of the solution is measured at 550 mμ. The amount of aluminium is obtained from the calibration curve prepared preliminarily. The blank test is carried out with the same procedure as in the sample after adding with a small amount of iron solution free from aluminium, in order to effect good separation of methyl isobutyl ketone from the acid solution.

V. Analytical result

1. Analysis with synthetic sample

Aluminium determination was carried out with a synthetic sample according to the analytical procedures described above, and the results are given in Table 5. Electrolytic iron was used and the determination was carried out after twice extractions with 30 ml of methyl isobutyl ketone when the amount of iron was 1 g. A fraction of 20 ml was taken from 100 ml and, since 0.2 g of electrolytic iron contained 3.7 μg of aluminium, this value was substracted from the amount of aluminium detected.

2. Analysis with actual sample

Results obtained from the determination of aluminium with several samples of iron and steel by the present method are listed in Table 6. In these experiments, 0.5 g of the sample was taken, and the determination was carried out on 1/10 to 2/10 of the solution. For the gravimetric method, 3~5 g of a sample was used, majority of iron was separated by extraction with methyl isobutyl ketone, and aluminium was determined by the usual oxine method (gravimetry) after separation with sodium hydroxide. As will be seen from this table, a well-agreeing result was obtained by these two methods.

Table 5. Results of determination of Al in synthetic samples.

Elements taken (mg)	Al added (μg)	Absorbance against blank	Al found (μg)	Error (μg)
Fe 1000	50	0.245 0.249 0.239	48.8 49.5 47.5	−1.2 −0.5 −2.5
Fe 1000 Mn 6.7	25	0.135 0.131 0.133	25.1 25.0 25.0	+0.1 0 0
Fe 500 Mn 6.7 Mo 8.9 Cu 5.0	50	0.263 0.265 0.261	52.0 52.5 51.5	+2.0 +2.5 +1.5

Table 6. Results of determination of Al in iron and steel samples.

Sample	Absorbance against blank	Al found		Conventional method (%)
		(μg)	(%)	
Electrolytic iron	0.039 0.042	3.0 3.2	0.003 0.003	—
Cast iron A	0.245 0.259	12.5 13.3	0.025 0.027	0.027*
Cast iron B	0.197 0.192	10.3 10.0	0.020 0.021	0.020**
Steel A	0.277 0.282	14.2 14.5	0.014 0.015	0.015**
Steel B	0.079 0.074	5.0 4.8	0.005 0.005	0.006**
Cr-steel	0.103 0.115	6.1 6.5	0.006* 0.007*	0.007*
Ni-Cr-steel	0.070 0.065	4.5 4.3	0.005* 0.004*	0.004*
Fe-Mo-steel	0.325 0.330	16.1 16.3	0.081 0.082	0.082*

* The results of Cr-steel and Ni-Cr-steel were obtained from both this method and conventional aluminon method after separation by mercuric cathode electrolysis.

** These results are obtained from the conventional oxine gravimetric method after extraction of the most of iron from solution of 3～5 g sample by methyl isobutyl ketone.

Summary

(1) Photometric determination of a micro-amount of aluminium was attempted by the use of chrome azurol S, a complexometric titration indicator for aluminium, copper, and zirconium. Some fundamental experiments were carried out and

a new analytical procedure was devised. By this method, majority of iron was removed by extraction with methly isobutyl ketone, copper and residual iron are masked by thioglycolic acid, the solution is adjusted to pH 5.6~6.8, and absorbance of the blue solution of aluminium chelate compound is measured at 550 mμ.

(2) This method requires addition of only a few reagents and does not necessitate warming at the time of coloration, as in the aluminon method, or the use of a protective colloid. Consequently, the procedure is simple and of extremely sensitive reaction for a micro-amount of aluminium; 0.002~0.1 per cent of aluminium can be determined with good reproducibility.